Fuel Processing Technology 110 (2013) 197–205

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Influence of temperature on liquid products yield of oil palm shell via subcritical water liquefaction in the presence of alkali catalyst

Hossein Mazaheri [a,b], Keat Teong Lee [a], Abdul Rahman Mohamed [a,*]

[a] School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia
[b] Department of Chemical Engineering, Faculty of Engineering, Islamic Azad University, Arak Branch, Arak, Iran

ARTICLE INFO

Article history:
Received 16 June 2012
Received in revised form 17 December 2012
Accepted 26 December 2012
Available online 27 January 2013

Keywords:
Subcritical
Oil palm shell (OPS)
Liquefaction
Bio-oil
Alkali catalysts
Thermogravimetric analyses

ABSTRACT

Oil palm shell (OPS) was converted to various liquid products through subcritical water liquefaction using a high-pressure autoclave reactor with and without the presence of K_2CO_3, Na_2CO_3, or NaOH as alkali catalyst at a temperature ranging from 483 to 603 K. Liquid products obtained were sub-classified to bio-oil and water soluble. In the absence of any catalyst, conversion of solid OPS increased from 44.5% to 65.8% as temperature rises from 483 to 603 K which is equivalent to the amount of hemicellulose and cellulose available in the OPS used (it has complete consistency with thermogravimetric analyses). However, with the addition of alkali catalyst, solid conversion and liquid product yield increased significantly. The use of 10% K_2CO_3 and 10% Na_2CO_3 gave almost similar results while the addition of 10% NaOH resulted to the highest solid conversion and liquid product at 84% and 53.4% respectively. In addition, the use of 10% NaOH also resulted to significantly lower gaseous product as compared to those with either other catalysts or without any catalyst at similar condition. The liquid product yield obtained is two times more than those obtained via the use of pure water subcritical liquefaction.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Today, the world society is confronting to serious and strategic problems such as environmental pollution, global climate change, rising energy prices, depletion of limited fossil fuel resources, and dependency on limited oil exported countries because of increasing fossil energy consumption. Therefore, it is necessary to look for and develop the future alternative fuels' resources due to the environmental problems.

There are various alternative energy resources available at present, encompassing hydro, biomass, wind, solar, hydrogen, and nuclear energy. Among these, biomass, which is an important resource convertible in energy, has been the subject of interest recently. In particular, forestry wasted and agriculture residues are the oldest and most useful resources of energy from which humans acquired energy traditionally. Besides that, owing to its wide availability in many parts of the world, biomass is popular internationally. Using indigenous sources of biomass for energy supply can avoid monopoly of markets by certain countries. Furthermore, the use of biomass as a substitute for fossil fuels can reduce the carbon content in the atmosphere as carbon dioxide is absorbed by plants via photosynthesis during their growth [1].

Thus, biomass is currently the fourth largest source of energy in the world. At present, this energy source supplies about 1185.84 million TOEs (Mtoe), consisting around 12.9% of the world's annual energy consumption. This portion is higher than that contributed by coal but is comparable to that contributed by gas and electricity [2]. Biomass is constituted mainly of forestry waste, energy crops, aquatic and waste biomass, and agricultural residues [3].

Thermochemical conversion using subcritical to supercritical liquefaction is one of the methods to convert biomass into liquid products (LPs). Thus, some researchers have recently liquefied some lignocelluloses (various types of biomass) using subcritical to supercritical fluid with or without catalysts [4]. The methods used include rapid hydrolysis of cellulose in subcritical and supercritical water (SCW) without the addition of any catalyst, conversion of lignocelluloses into bioenergy and chemicals using supercritical fluid technology, and catalytic hydrothermal treatment of woody biomass in the presence of K_2CO_3 with different concentrations and biomass/water ratio [5–8].

In the work of Ehara and Saka, ether and ester linkages of woody biomass were instantly hydrolyzed in subcritical or supercritical water [9]. Furthermore, Qianand Cheng have investigated the effects of temperature and reaction time on product distribution and yields of chemical products by subjecting switchgrass to subcritical water [10,11]. Moreover, Qian also showed that the main liquefied product was significantly influenced by the process condition in direct liquefaction of woody biomass by water with Na_2CO_3 as a catalyst in an autoclave [11]. Wahyudiono et al. demonstrated that with increasing reaction time of lignin degradation in near supercritical water process, the amount of higher molecular weight fractions decreased while the amount of lower molecular weight fractions increased [12].

---

* Corresponding author. Tel.: +60 4 5996410; fax: +60 4 5941013.
E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

0378-3820/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fuproc.2012.12.015

Among all conversion methods, thermochemical liquefaction in subcritical water has enticed many scientists' attentions recently because this process could eliminate the sample pre-treatment step and reduce reaction time while achieving high liquefaction efficiency as in the conventional process such as pyrolysis [13]. Subcritical water is defined as liquid water at temperatures between the boiling point and the near critical point (373–647 K), which is appropriately used as a medium for organic chemistry reactions [14].

Subcritical water exhibits properties that are very different from those of ambient liquid water. For instance, subcritical water has a lower dielectric constant, weaker hydrogen bonds and a higher isothermal compressibility than ambient liquid water. These properties make subcritical water a very promising reaction medium for conversion of biomass such as lignocellulosic materials. It has the ability to break the rigid structure of lignocelluloses and consequently, decompose the lignocellulosic materials into smaller components by hydrolysis and further reactions [14,15]. Thus, subcritical water liquefaction has been widely employed for an efficient production of liquid bio-oil and valuable chemicals from wasted biomass.

Actively promoting agricultural activities, Malaysia is a country abounding in biomass wastes. Being one of the main palm oil producing and exporting countries in the world, oil palm is treated as one of its most important agriculture crops. In 2009, 4.88 million ha of land in Malaysia was covered by oil palm cultivation; producing 90.40 million tons of fresh fruit bunches (FFB). The amount of oil palm biomass produced by these oil palm plantations in that year was estimated to be about 37.0 million tons, consisting of 5.5% of shell [16,17]. It has been proven that biomass sources can become an economical source of renewable energy. Besides that, it is also undisputed that indiscriminate disposal of these wastes would result in serious environmental problems. Thus, developing new technologies to convert oil palm biomass into energy sources (liquid or gas) becomes an attractive field of research.

In our previous study, we have reported the conversion of oil palm fruit press fiber (FPF) to biofuel using subcritical water liquefaction and using supercritical organic solvent [3,4]. However, in this work, this article underlines the study of alkali catalysts' effects on the efficiency of using subcritical water to decompose oil palm shell (OPS) into various liquid and residual solid waste products. The decomposition of OPS was carried out in a high-pressure batch reactor with and without the presence of catalyst such as K_2CO_3, Na_2CO_3, and NaOH.

2. Methods

The OPS was taken from one of the oil palm mills in Malaysia. The air-dried OPS were grounded and screened. Only the portion with particles size between710 and 1000 μm was used. Then, the OPS elements were analyzed. The structural analysis was carried out according to the Technical Association of the Pulp and Paper Industry standard (TAPPI's) test methods whereas the element analysis (e.g. CHNS/O) was implemented with CHNS/O analyzer (Series Π CHNS/O Analyzer 2400). The results are tabulated in Table 1. This table shows that oil palm shell (OPS) contain relatively high extractive matter content. The elemental compositions of the liquid products (WS and Bio-Oil) were also analyzed in the same manner as the raw OPS. In addition, in order to explicate the effect of subcritical water treatments on decomposition of hemicellulose, cellulose, and lignin of OPS, the solid residual of runs was also analyzed in the Thermogravimetric Analyzer (TA Instrument, SDT Q600). Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) profiles of pristine OPS and solid residual of runs were obtained by heating under nitrogen gas with heating flow rate of 20 °C/min.

Water in the presence and absence of 10% catalyst (i.e. potassium carbonate, sodium carbonate, and sodium hydroxide) was used respectively in the experiments. For each run, the reactor was heated from room temperature to the desired temperature. All the subcritical experimental runs were performed using 10 g of air dried OPS by varying temperatures between 483 and 603 K. Experiments were conducted in a 450 ml high-pressure autoclave reactor (supplied by Buchi Glas Uster, Model “Limbo Li” Switzerland).

In a typical run, 10 g of air dried OPS powder (710 to 1000 μm) and 100 ml of water or solution with a desired amount of catalyst were loaded into the autoclave reactor which was then plugged with ten screw bolts. Subsequently, the reactor was purged with nitrogen gas (purification) to remove any residual air and to increase the reactor pressure to 10 bars. The heat supply to the reactor was provided by an external jacket heater, in which the power was adjusted to give an approximate heating time of 45 min. The temperature of the high-pressure vessel was measured using an iron-constantan thermocouple and the temperature was controlled at the desired level for 60 min [18]. After each run, the gas was vented. The gas products were not analyzed in this work as our main interest was the liquid products. Moreover, from a thermodynamics point-of-view, gasification process normally leads to similar gas compositions containing CH_4, CO_2, CO and H_2 [19]. The solid and LPs were separated from the autoclave into a beaker. Finally, the oil and solid residues were removed from the autoclave by washing them with used solvents. The liquid soluble product from the reactor consists of polar or aqueous phase containing organo-oxygen compounds with low molecular weight, and a non-polar or non-aqueous phase containing insoluble organics (mainly aromatics and organic compounds) with high molecular weight. The former is called water soluble whereas the latter is called bio-oil, heavy oil. It is noteworthy that the latter have limited solubility in diethyl ether, diethyl acetate, and acetone. Based on the polarity of solvents, diethyl ether, diethyl acetate, and acetone were used as the solvents to extract the components of liquid soluble products. The products taken out from the reactor had been filtered with filter paper under vacuum for 10 min to separate the solid and LPs. During filtration, 50 ml of diethyl ether solvent was used to wash the solid products. The filtrate was then extracted with diethyl ether by using liquid–liquid extraction procedure in a separatory funnel. The two portions obtained through this separation are called water-soluble and diethyl ether soluble products. Water and diethyl ether were removed from the two portions separately using rotary evaporator system (Büchi Rotavapor R-215) under reduced pressure, and the remaining fractions were weighed and designated as water solution (WS) and diethyl ether soluble (DES) products, respectively. In the same manner, the solid residue and water solution were also extracted using diethyl acetate. After removal of diethyl acetate from water using a rotary evaporator under reduced pressure, the fractions were weighed and designated as diethyl acetate soluble (DAS) and water soluble (WS) products, respectively.

Likewise, the solid residue was also washed using acetone. After removal of acetone using a rotary evaporator under reduced pressure, the fractions were weighed and designated as acetone soluble (AS) products. Finally, the acetone insoluble fraction was dried until constant weight was recorded in an oven at 378 K, called the solid residue including unconverted OPS.

Table 1
Chemical and elemental analysis of oil palm shell (wt.% of dry basis).

Cellulose	Hemicelluloses	Lignin	Extractives[a]	Moisture	Carbon	Hydrogen	Oxygen	Nitrogen
39.7	21.8	32.5	6.0	7.5	50.01	7.66	29.02	13.31

[a] Soxhelet extractives were obtained by using ethanol–toluene (2/1, v/v).

All yields were calculated on a dry basis and were assumed ash-free. Liquid products including water soluble (WS), and bio-oil, tar or heavy products (including DES, DAS and AS) obtained from subcritical water liquefaction of OPS were analyzed by GC–Mass spectrometer equipped with a mass selective detector (GC–MS; Clarus 600T; Perkin Elmer).

The results obtained in this study are reported using the parameters defined as:

$$Conversion(\mathrm{wt.\%}) = \left(1 - \frac{W_{AI}}{W_{Dry\ \ OPS}}\right) \times 100 \tag{1}$$

$$Liquid\ \ product\ \ yield(\mathrm{wt.\%}) = \left(\frac{W_{LP}}{W_{Dry\ \ OPS}}\right) \times 100 \tag{2}$$

$$Gaseous\ \ product\ \ yield(\mathrm{wt.\%}) = \left(1 - \frac{W_{LP}}{W_{Dry\ \ OPS}}\right) \times 100 \tag{3}$$

$$Residue\ \ yield(\mathrm{wt.\%}) = \left(\frac{W_{Dry\ \ AI}}{W_{Dry\ \ OPS}}\right) \times 100 \tag{4}$$

$$Bio\_oil = AS + DAS + DES \tag{5}$$

$$LP(Liquid\ \ Product) = Bio\_oil + WS. \tag{6}$$

Where,

AI	Acetone insoluble product (dry and wet, g)
AS	Acetone soluble product (g)
DAS	Diethyl- acetate soluble product (g)
DES	Diethyl- ether soluble product (g)
WS	Water-soluble product (g)
SR	Solid residue (dried acetone insoluble product) (g).

In addition, the high heating value (HHV) in (MJ/kg) of the liquid products was computed from the Dulong formula [20]:

$$HHV\left({}^{MJ}\!/_{kg}\right) = 0.3383\ \ C + 1.442(H - 0/8) \tag{7}$$

where C, H and O are the weight percentages of carbon, hydrogen and oxygen, respectively.

3. Results and discussion

3.1. Liquefaction of OPS in pure subcritical water

Initially, the OPS was subjected to pure subcritical water with reaction temperature ranging from 483 to 603 K. Fig. 1 shows that the conversion of OPS to liquid and gaseous products was achieved. OPS decomposition started at a reaction temperature lower than 483 K.

From this figure it can be seen that at 483 K, 45% of OPS was converted to liquid/gaseous products, which is almost equal to all hemicellulose and a major part of cellulose available in OPS. Therefore, it seems that in the pure water liquefaction treatment, all the hemicellulose and a major part of cellulose available in the OPS were converted before the temperature reached 483 K and when temperature was increased to 603 K, almost all the remaining cellulose in OPS would be converted. This is because hemicellulose is in amorphous form, whereas cellulose is in crystalline form. Therefore, hemicelluloses are less thermally stable than cellulose. Furthermore, in the pure water liquefaction treatment, when temperature was increased from 483 to 603 K, the conversion of OPS increased slightly from 45.0% to 65.8% corresponding to the amount of hemicellulose and cellulose in OPS. This suggests that cellulose hydrolysis takes place via subcritical water treatment at temperature ranging from 483 to 603 K.

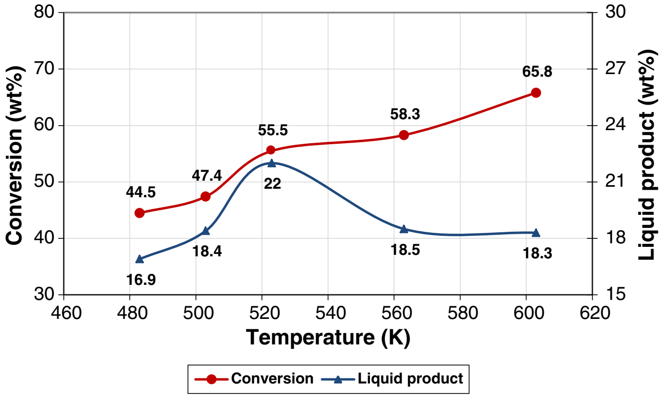

Fig. 1. Effect of temperature on conversion and liquid product yield from subjecting OPS to pure subcritical water liquefaction at different temperatures.

At an elevated temperature, i.e. beyond the boiling point of water and below its critical point, the ionic characterization of water increases, thereby transforming water into an acid/base precursor that can catalyze various ionic reactions. Apart from that, subcritical water at this region can be used not only in various synthesis reactions but also some degradation reactions such as biomass liquefaction. In fact, subcritical water accelerates biomass depolymerization by hydrolysis. The glycosidic bond of cellulose and hemicellulose is polar and is therefore hydrolyzed very rapidly in water at subcritical condition. The cellulose and hemicellulose compounds are broken down into smaller sugar units that eventually resort to collapse of the entire biomass structure. On the contrary, at low temperature, the conversion rate of glucose or oligomer is much faster than the hydrolysis rate of cellulose. Therefore, even the hydrolysis of cellulose products such as glucose or oligomer has taken place, further decomposition occurs so rapidly that the high yield of hydrolysis products cannot be obtained [21–23].

In other words, the OPS has been successfully converted to LPs/gaseous after being subjected to subcritical water. These conclusions are further confirmed by the thermogravimetric (TG) and derivative thermogravimetric (DTG) data. The TG and DTG plots for OPS solid residue of experiment runs, along with the pristine OPS as a reference are shown in Fig. 2. The results demonstrate that thermal degradation of pristine OPS takes place through three step processes with a significant decomposition over than 500 K and a gradual mass loss as the temperature reaches to 650 K. Pristine OPS starts to decompose at about 420 K, which the temperature is shifted to higher values for OPS solid residues of subcritical treatment. In fact, DTG plot of pristine OPS shows that there is an earlier weight loss at around 420 K, suggesting the presence of a small amount of extractive compounds. The hemicellulose and cellulose have higher temperature stability, with the maximum weight loss occurring at around 500 K, demonstrating the higher crystalline quality of the cellulose in the pristine OPS. Because of this, as shown in Fig. 2, the peak that appeared in the DTG curve is high.

As can be seen from the figure, there are two peaks in the DTG cures of pristine OPS as temperature increases between 510 and 650 K. In fact, following the earlier decomposition another two peaks in the DTG curve are seen at around 510 and 600 K, exhibiting the hemicellulose and cellulose decomposition peaks, respectively [24]. It can be seen from Fig. 2; the lignin exhibits higher thermal stability, which weight loss occurring at around 650 K, reflecting the highest stability of the lignin in the pristine OPS.

From Fig. 2, it is clear that thermal degradation of OPS solid residue (subcritical water treatment at 480 K) takes place through two step processes that consist of a maximum decomposition temperature over

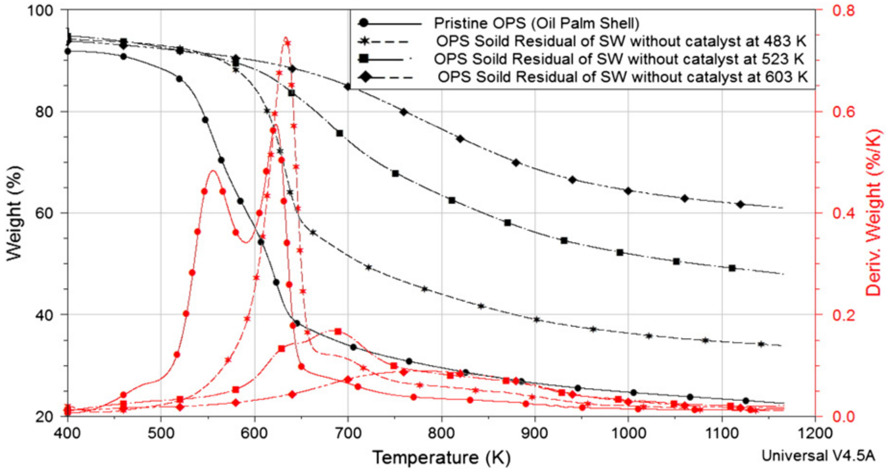

Fig. 2. Derivative thermogravimetric (DTG) curves of and pristine OPS and solids residue from pure subcritical water liquefaction at different temperatures.

than 550 K and a gradual mass loss as the temperature reaches 650 K, which exhibits the temperature stability of the cellulose and higher temperature stability of lignin in OPS solid residue, respectively. Fig. 2 also indicates that thermal degradation of other OPS solid residues (subcritical treatment at 523 and 603 K) takes place through two step processes too, that consist of a proportional gentle decomposition temperature over than 650 K and a slight weight loss as the temperature reaches 725 K, which exhibits the stability of lignin in OPS solid residues.

Table 2 presents the selectivity of LPs based on solvent solubility. In Table 2, it can be seen that the OPS has been successfully converted into LPs after being subjected to subcritical water. The percent of conversion ranged from 44.5% to 65.8% when the reaction temperature was increased from 483 to 603 K. For instance, the result shows that at 483 K, 44.5% of OPS was converted. It is also inferable that all hemicellulose and a major part of cellulose present in the OPS were converted before reaching the temperature of 483 K. When temperature was further increased from 483 K to 603 K, the cellulose remaining in the OPS (about 20%) was then converted. Thus, as the temperature rose from 483 K to 603 K, the conversion of OPS also soared from 44.5% to 65% corresponding to the amount of hemicellulose and cellulose present in OPS. In other words, the OPS has been successfully converted to gaseous/LPs after being subjected to subcritical water. This suggests that cellulose hydrolysis takes place via subcritical water treatment at temperature ranging from 483 to 603 K. This can be attributed to the decomposition of intramolecular and intermolecular hydrogen bonding in the cellulose present in the OPS.

Table 2
Solid residue, liquid and gaseous products obtained by subcritical water liquefaction of OPS in the presence and in the absence of catalyst at different temperatures.

Temperature (K)	Kind of catalyst	Solid residue (wt.%)	Liquid product (wt.%)	Gaseous products (wt.%)
483	No catalyst	55.50	16.9	27.6
	10% K_2CO_3	55.90	28.5	15.6
	10% Na_2CO_3	55.30	27.3	17.4
	10% NaOH	56.30	38.6	5.10
503	No catalyst	52.50	18.4	29.1
	10% K_2CO_3	44.90	32.1	23.0
	10% Na_2CO_3	45.80	32.9	21.3
	10% NaOH	42.10	41.9	16.0
523	No catalyst	44.20	22	33.8
	10% K_2CO_3	29.90	38.6	31.5
	10% Na_2CO_3	27.70	42.9	29.4
	10% NaOH	24.10	49	26.9
563	No catalyst	41.70	19.3	39.0
	10% K_2CO_3	18.70	47.9	33.4
	10% Na_2CO_3	18.50	47	34.5
	10% NaOH	16.90	53.4	29.7
603	No catalyst	34.20	18.3	47.5
	10% K_2CO_3	18.10	40.5	41.4
	10% Na_2CO_3	16.10	40.9	43.0
	10% NaOH	16.20	47.9	35.9

In order to study the effects of temperature and catalysts on the reaction, the LP distributions at different temperatures in the presence and absence of the catalysts were investigated. Results shown that the LP yield (particularly WS product) increased slightly when the reaction temperature was rose from 483 K to 523 K. Subsequently, the yield began to drop with further temperature rise. Contrarily, the bio-oil compounds started to increase gradually when the reaction temperature increases from 563 to 603 K with gradual increase in the gaseous products' (GP) yield (Table 2). This is because some of the LPs had been converted to gaseous products as discussed earlier. This finding indicates that the decomposition of OPS at subcritical water is very dependent on temperature. Although a higher temperature leads to a higher solid conversion, it does not necessarily result in higher liquid yields as shown in Fig. 1. This is because over 523 K, the decomposition rate of LPs was much faster than the hydrolysis rate of OPS. Therefore, if the objective is to maximize the LPs, a temperature of 523 K would be the optimum operating condition. However, if the objective is to maximize the solid conversion, a higher reaction temperature would be more favorable. With increasing temperature, condensation reaction is enhanced leading to thermal decompositions of OPS to volatiles. This result shows that the yields of gaseous products (GP) at 603 K were much higher than those of 563 K. This finding becomes more evident if experimental results of subcritical water liquefaction are analyzed in the presence of K_2CO_3, Na_2CO_3, and NaOH as catalysts at the same condition in the following sections.

3.2. Influence of catalyst on decomposition of OPS in subcritical water liquefaction

For the decomposition of OPS via pure subcritical water liquefaction, the WS and bio-oil yields show relatively low values ranging from 6.4% to 8.4% and 10.5% to 14.2%, respectively, by increasing the temperature from 483 to 603 K. These values are too low, rendering this process uneconomical in terms of yield and selectivity. Hence, in order to increase the LP yield, some catalysts need to be introduced. Consequently, in this work, the influences of alkali catalysts such as K_2CO_3, Na_2CO_3, and NaOH on the decomposition of OPS using subcritical liquefaction at the same conditions were investigated.

3.2.1. Influence of K_2CO_3 and Na_2CO_3

In order to investigate the effects of K_2CO_3 and Na_2CO_3 on the decomposition of OPS at subcritical water condition, the product distributions were analyzed after the addition of 10% K_2CO_3 or 10% Na_2CO_3 as the catalyst. Figs. 3 and 4 portray the solid conversion and the liquid product yields accomplished by subjecting the OPS to subcritical water liquefaction with 10% K_2CO_3 or 10% Na_2CO_3 as the catalyst at different temperatures. Besides, Tables 2 and 3 exhibit the conversion and selectivity of solvent soluble product distributions obtained via subcritical water liquefaction in the presence of 10% K_2CO_3 and 10% Na_2CO_3 at different temperatures, respectively.

In this work, by comparing the results from the use of 10% K_2CO_3 and 10% Na_2CO_3, the solid conversion, LPs, gaseous product, and solid residue for both cases are found to be almost similar as shown in Figs. 3 and 4. When K_2CO_3 or Na_2CO_3 was added to the process of subcritical water liquefaction, the OPS conversion increased from 44.10% to 81.90% and 44.7% to 83.90% with a temperature rise from 483 K to 603 K respectively.

Meanwhile, the addition of K_2CO_3 or $NaCO_3$ corresponded to an escalation of bio-oil product yield to 32.10% and 29.10% respectively. Likewise, an increase of WS product yield to 15.80% and 20.5% was also observed from the addition of K_2CO_3 and $NaCO_3$, respectively. These results indicate that the LP yield rose from 28.5% to 47.90% and from 27.30% to 47.00%, which is almost twofold of that, obtained using pure subcritical water in the presence of K_2CO_3 or Na_2CO_3 as the catalyst.

In this study, while the solid conversion increases dramatically, the amount of solid residue and gaseous product lessens noticeably if compared to that obtained via pure subcritical water liquefaction of OPS with a temperature rise from 483 K to 603 K. However, the addition of catalyst entails an increase in the yield of LP (WS and bio-oil products). This directly indicates the feasibility of obtaining a higher yield of LP by employing a small amount of K_2CO_3 or Na_2CO_3 via subcritical water liquefaction treatment. Nevertheless, it is also observed that during catalytic subcritical water treatment at a temperature above 563 K, there is a competition between the gasification and liquefaction processes to the extent that the slopes of LP reduction rate and GP increase rate are almost equal. The reduction of LP yield in the presence of K_2CO_3 or Na_2CO_3 catalyst is due to the cracking of LPs to gaseous products by isomerization, dehydration, and fragmentation. When the OPS is heated to temperature above 563 K, its glycosidic linkages are weakened leading to cleavages of the molecules into smaller fragments. In other words, with K_2CO_3 or Na_2CO_3 catalyst, the decomposition of LP to gaseous compounds may take place. On the other hand, the presence of K_2CO_3 or Na_2CO_3 as a catalyst at a temperature above 523 K resorts to breakdown of large molecules in the liquid phase, giving rise to smaller molecules which enrich the gaseous phase. Therefore, a decrease in the LP yield was observed at a temperature above 523 K in the presence of K_2CO_3 or Na_2CO_3 relative to that obtained by pure subcritical water liquefaction of OPS.

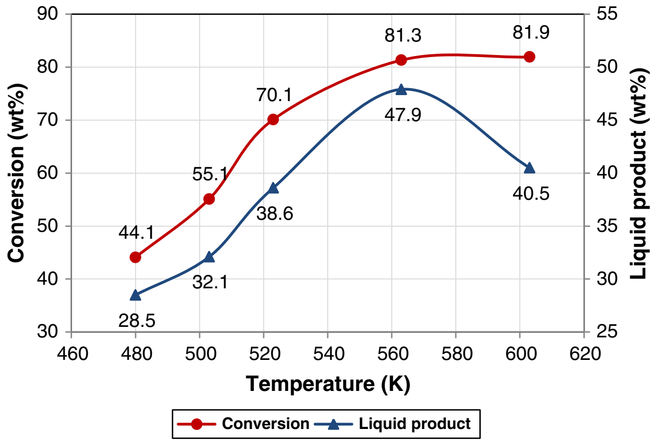

Fig. 3. Effect of temperature on conversion and liquid product yield from subjecting OPS to subcritical water liquefaction with 10% K_2CO_3 as catalyst at different temperatures.

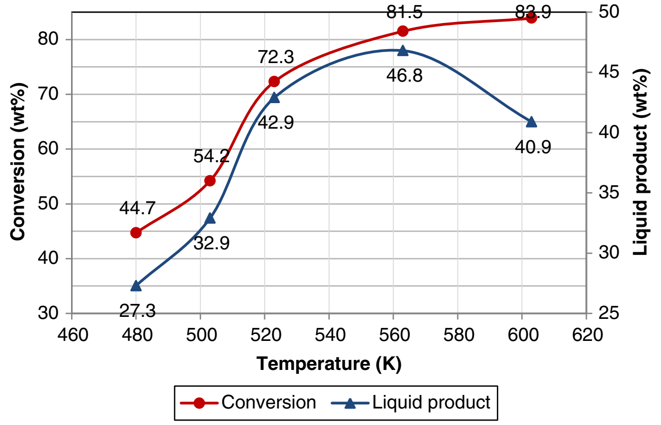

Fig. 4. Effect of temperature on conversion and liquid product yield from subjecting OPS to subcritical water liquefaction with 10% Na_2CO_3 as catalyst at different temperatures.

Thermal degradation of OPS solid residue from subcritical water liquefaction (SW) in the presence of 10% K_2CO_3 and 10% Na_2CO_3 as a catalyst at the different temperatures is shown in Figs. 5 and 6, respectively. As can be seen, the TG and DTG plots of OPS solid residue from subcritical water liquefaction (SW) in the presence of 10% K_2CO_3 and 10% Na_2CO_3 is very similar. The virgin OPS is also tested as references and shown in these figures.

From the figures, TG and DTG show that the decomposition of OPS solid residue from subcritical water treatment in the presence of 10% K_2CO_3 and 10% Na_2CO_3 at 483 K starts at around 550 K. The degradation in these cases takes place in two stages. At the first stage, the weight decreases due to cellulose decomposition within temperature ranges from 525 to 650 K. Afterwards, the gradual mass loss occurs at the second stage due to lignin decomposition within wide temperature range. Lignin decomposition rate becomes slower than that of

Table 3
The selectivity of solvents soluble product distributions obtained by subcritical water liquefaction of OPS in the presence and in the absence of catalyst at different temperatures.

Temperature (K)	Kind of catalyst	LP yield (wt.%)		AS[b]	DAS[c]	DES[d]
		WS[a]	Bio-oil			
483	No catalyst	6.4	10.5	4.5	4.5	1.5
	10% K_2CO_3	14.0	14.5	8.0	5.0	1.5
	10% Na_2CO_3	13.7	13.6	6.1	5.5	2.0
	10% NaOH	27.5	11.1	7.0	3.6	0.5
503	No catalyst	6.5	11.9	4.7	6.0	1.2
	10% K_2CO_3	13.6	18.5	9.2	7.3	2.0
	10% Na_2CO_3	16.3	16.6	8.3	6.1	2.2
	10% NaOH	21.8	20.1	11.0	6.0	3.1
523	No catalyst	8.4	13.6	6.1	6.0	1.5
	10% K_2CO_3	15.4	23.2	13.0	7.2	3.0
	10% Na_2CO_3	20.5	22.4	12.5	7.2	2.7
	10% NaOH	24.4	24.6	12.7	7.4	4.5
563	No catalyst	6.7	11.8	3.8	6.0	2.0
	10% K_2CO_3	15.8	32.1	17.6	9.0	5.5
	10% Na_2CO_3	17.7	29.1	14.3	6.5	8.3
	10% NaOH	25.1	28.3	17.3	7.9	3.1
603	No catalyst	4.1	14.2	3.8	7.3	3.1
	10% K_2CO_3	12.6	27.9	5.1	8.1	14.7
	10% Na_2CO_3	14.5	26.4	8.0	8.2	10.2
	10% NaOH	24.0	23.9	7.6	7.3	9.0

[a] WS: Water-soluble products.
[b] AS: Acetone soluble products.
[c] DAS: Diethyl acetate soluble products.
[d] DES: Diethyl- ether soluble products.

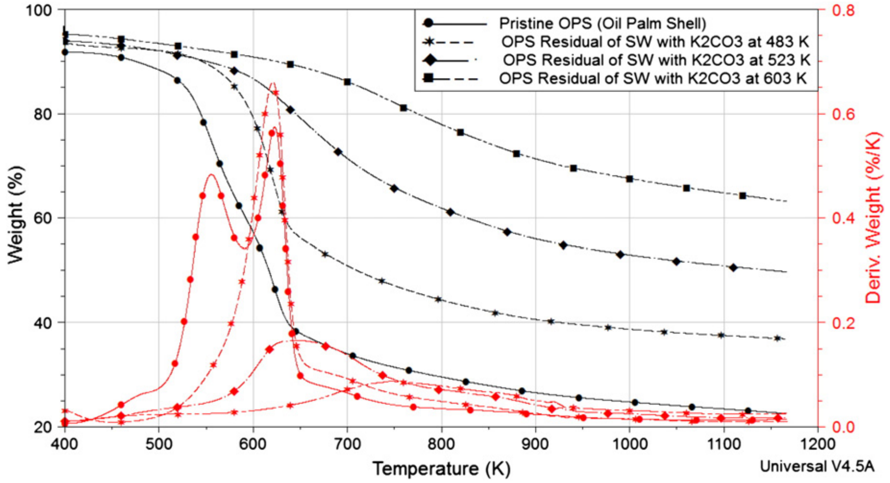

Fig. 5. Derivative thermogravimetric (DTG) curves of and pristine OPS and solids residue from subcritical water liquefaction with 10% K_2CO_3 as catalyst at different temperatures.

the cellulose decomposition degradation. Comparing TG and DTG curves for the OPS solid residue from subcritical water treatment in the presence of 10% K_2CO_3 and 10% Na_2CO_3 at 483 K with those for the virgin OPS, all the extractive compounds and the hemicellulose in the virgin OPS almost decompose in the subcritical water treatment in the presence of 10% K_2CO_3 and 10% Na_2CO_3 at temperature 483 K. This is because the virgin OPS decomposition takes place in three main stages as shown in Figs. 5 and 6.

The distributions of TG and DTG of OPS solid residue from subcritical water treatment in the presence of 10% K_2CO_3 and 10% Na_2CO_3 at 523 K and 603 K are also displayed in Figs. 5 and 6. As can be seen from the figures, there is an obvious discrepancy between the curves; with only one peak in the derivative thermogravimetric (DTG) curve. This suggests that the peak is caused by a small relatively amount of cellulose chemicals and lignin, which have a particularly higher thermal stability.

As a conclusion, the results indicated that the LPs' (WS and bio-oil compounds) yield from subcritical water liquefaction by using K_2CO_3 and Na_2CO_3 as the catalyst is higher than those obtained by using pure subcritical water when temperature changed from 483 to 603 K as shown in Fig. 10. This is possibly attributed to the reduction reactions, as well as cracking reactions which might occur during subcritical liquefaction in the presence of K_2CO_3 or Na_2CO_3 above the temperature limit. In addition, results show that the yield of gaseous products from subcritical liquefaction in the presence of K_2CO_3 or Na_2CO_3 was less than that from non-catalytic subcritical liquefaction.

3.2.2. Influence of NaOH as catalyst

In the previous sections, the promising results of increased conversion and LP were acquired by utilizing K_2CO_3 or Na_2CO_3 as the catalyst. In this section, the effects of another alkali catalyst on the decomposition of OPS via subcritical water liquefaction were investigated by employing NaOH and maintaining the reaction period at 60 min.

The TG and DTG curves of OPS solid residues from subcritical treatment in the presence of 10% NaOH as a catalyst, which was obtained at 483, 523, and 603 K, are shown in Fig. 7. The virgin OPS is also tested as references and shown in Fig. 7. From the figure, it is clear that the DTG peaks differ in height and position. The peak height is directly proportional to the reactivity, while the temperature corresponding to peak height is inversely proportional to the reactivity [24]. Comparison between the DTG curves of the OPS solid residue from subcritical water treatment and the virgin OPS, all the extractive compounds and the hemicellulose in the virgin OPS almost decomposed in the subcritical water treatment in the presence of 10% NaOH at temperature 483 K. This is because the virgin OPS decomposition takes place in three main stages as shown in Fig. 7.

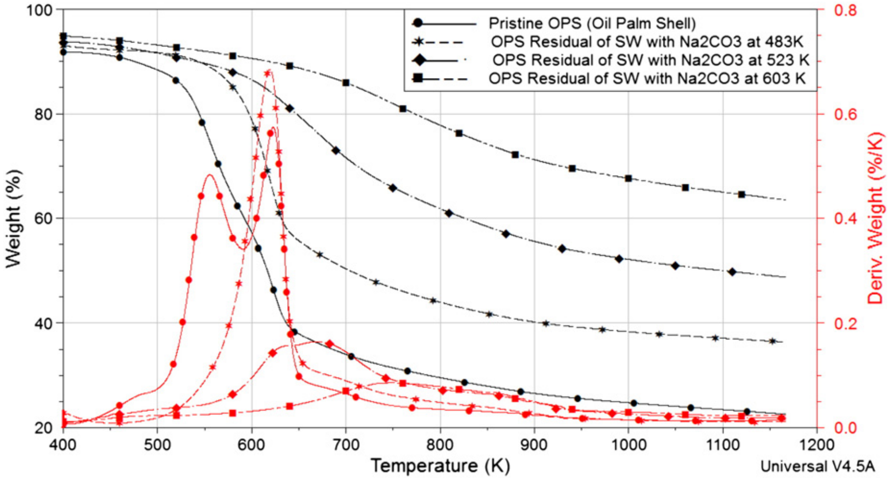

Fig. 6. Derivative thermogravimetric (DTG) curves of pristine OPS and solid residue from subcritical water liquefaction with 10% Na_2CO_3 as catalyst at different temperatures.

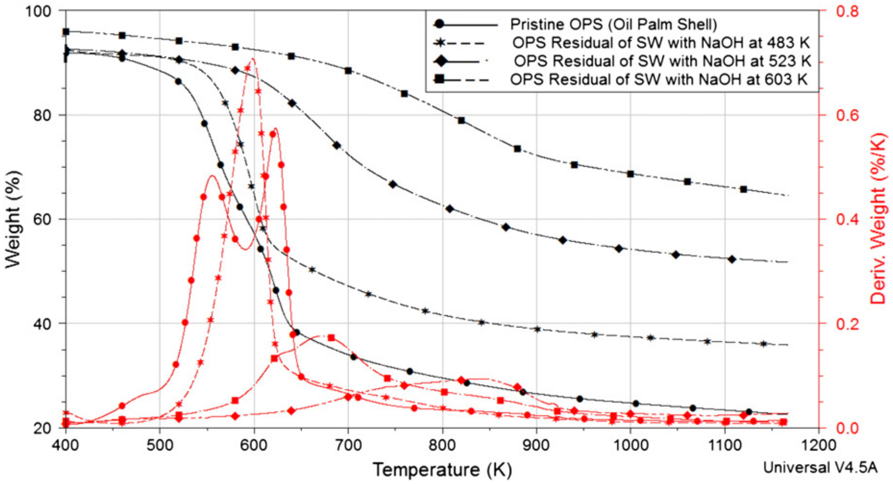

Fig. 7. Derivative thermogravimetric (DTG) curves of pristine OPS and solids residue from subcritical water liquefaction with 10% NaOH as catalyst at different temperatures.

Fig. 7 also indicates the TG and DTG plots of OPS solid residue from subcritical water treatment in the presence of 10% NaOH at 523 K and 603 K. As is illustrated by the figure, in contrast to virgin OPS, there is an obvious discrepancy between the curves; with only one peak in the derivative thermogravimetric (DTG) curve. This suggests that the peak is caused by a small relatively amount of cellulose compound and lignin, which have a particularly higher thermal stability. In other words, all the extractive compounds, hemicellulose and a major part of cellulose in the virgin OPS almost decomposed in the subcritical water treatment in the presence of 10% NaOH at temperature over 600 K. This is because the virgin OPS decomposition takes place in three main stages as shown in Fig. 7.

The experimental results obtained using NaOH as the catalyst is summarized in Fig. 8, Tables 2 and 3. Results show that the yields of LP and the conversion of OPS lies in the range of 38.6%–59.00%, and 53.30–83.80% respectively, increasing proportionally with the reaction temperature without any char production. Subsequently, as Table 3 presents, bio-oil and WS products varied from 11.10%–28.30% and 27.50%–24.00%, respectively as temperature increased from 483 to 603 K.

Figs. 9 and 10 show that there is a significant improvement in the conversion and LP yield as compared with those obtained by using either pure subcritical water, or subcritical water added with K_2CO_3 or Na_2CO_3. However, results indicated, higher liquid selectivity of WS products is obtained should NaOH be used in lieu of K_2CO_3 and Na_2CO_3. The product distributions for the case of NaOH are also presented in Tables 2 and 3. In Table 2, it can be seen that the gaseous product in the case of subcritical water treatment in the presence of NaOH is lower than other cases i.e. water subcritical treatment with or without K_2CO_3 and Na_2CO_3 as the catalyst, as a result of higher liquid product yield.

From results, it is inferable that the conversion of OPS in the presence of NaOH, Na_2CO_3, or K_2CO_3 as the catalyst via subcritical water liquefaction is nearly similar. However, the LP yield from the use of NaOH is higher than that from the use of Na_2CO_3 or K_2CO_3 and is significantly higher relative to the use of pure water. In fact, the LP yield in the presence of NaOH as the catalyst is more than twofold the LP yield obtained via pure water subcritical liquefaction. Results show that, the use of NaOH generates a dramatically lower amount of gaseous products compared to the use of other catalysts or the absence of any catalyst.

Fig. 9 and Fig. 10, show that the addition of alkali catalyst to the subcritical water treatment increased the solid conversion almost from 44.5% to 84% with a temperature rise from 483 K to 603 K. On the other hand, with an alkali catalyst, more than 15%, on average, of hemicellulose and cellulose present in the OPS was converted. This is tantamount to 50% of lignin available in the OPS to biomass structure without any char production following the addition of alkali catalyst to subcritical water treatment. This implies that lignin hydrolysis has taken place in the presence of alkali catalyst upon increasing the

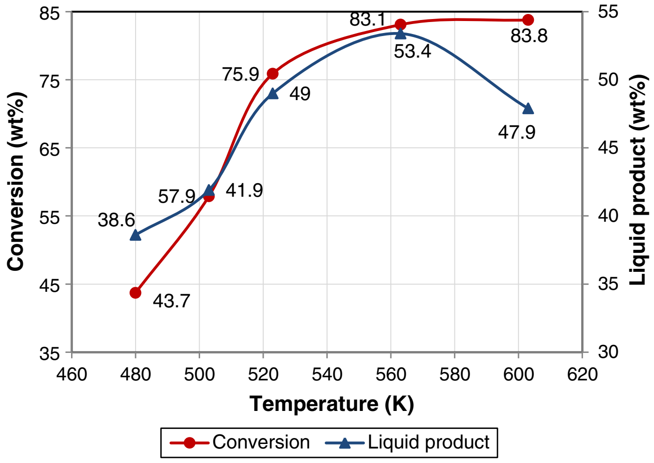

Fig. 8. Effect of temperature on conversion and liquid product yield from subjecting OPS to subcritical water liquefaction with 10% NaOH as catalyst at different temperatures.

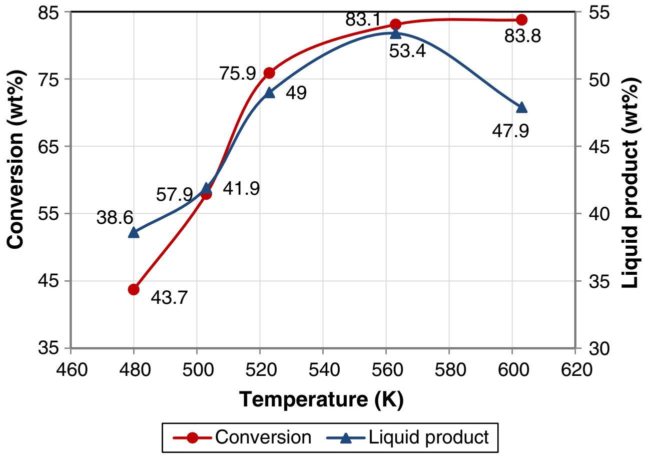

Fig. 9. Effect of catalysts on the conversion from subjecting OPS to subcritical water liquefaction at different temperatures.

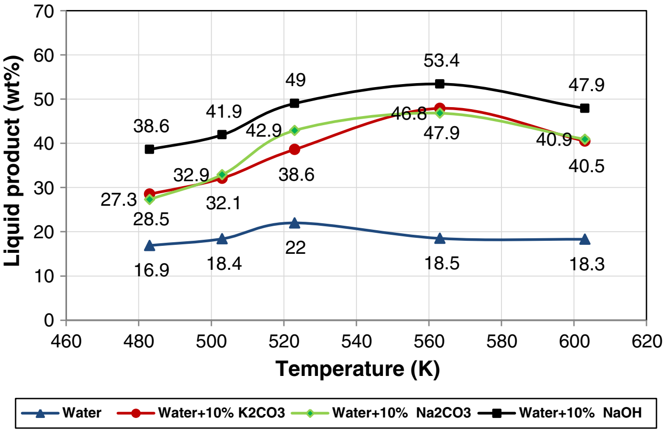

Fig. 10. Effect of catalysts on the LP yields from subjecting OPS to subcritical water liquefaction at different temperatures.

temperature to 603 K. This is probably attributed to the collapse of intramolecular and intermolecular hydrogen bonding in the OPS structure.

In addition, the result also shows that the LP yield, bio-oil compounds, and WS obtained via subcritical water liquefaction by using NaOH as the catalyst are higher than those obtained by using either pure subcritical water or Na_2CO_3 and K_2CO_3 catalyst. This might be due to the reduction reactions, as well as cracking reactions that occurred during subcritical liquefaction with NaOH. Besides that, the yield of gaseous products obtained from subcritical liquefaction in the presence NaOH is comparably less than that obtained from non-catalytic subcritical water or Na_2CO_3 and K_2CO_3 catalyzed treatment.

Furthermore, the use of alkaline catalysts such as NaOH seemingly prevents the formation of stable chemical structures. They weaken the C – C bond, thereby decreasing the activation energy for the complex reaction. It is assumed that the alkali catalyst triggers swelling of the OPS, leading to an increased internal surface area and a wider separation of structure linkages between holocellulose and lignin. However, a dilute NaOH catalyst renders weakening of the intermolecular interaction of the polymeric chain. This not only catalyzes the interlink dehydration but also promotes the processes of retroaldol cleavage and condensation of the products generated at the same time [25].

As a conclusion, the addition of NaOH effects the intermolecular interaction of the polymeric chain bonds (cellulose, hemicelluloses, and lignin bonds) and simultaneously brings about cleavage and condensation of the products. This can be substantiated by a drop in the amount of gaseous products from the OPS at subcritical water liquefaction condition. Consequently, based on the results presented, employing a small amount of sodium hydroxide as the catalyst is feasible to obtain high LP yields, bio-oil products, WS selectivity, conversion, and low GP from OPS decomposition compared to pure water subcritical treatment.

4. Liquid products

The OPS, water soluble and bio-oil liquid products obtained by subcritical water liquefaction of OPS at 603 K for 60 min with and without catalyst were analyzed with an elemental analyzer to determine their quantitative composition (C, H and N). Their composition and calculated HHV from Eq. (7) are tabulated in Table 4. In comparison to oil palm shell, the liquid products have similar composition and consequently similar HHV. It can be seen that various catalysts only slightly changed the composition and increased HHV of the bio-oil products. This is because the bio-oil contains much higher carbon concentration and lower oxygen content. As evidenced by GC/MS

Table 4
Elemental compositions of oil palm shell and liquid products obtained by subcritical water liquefaction of OPS at 603 K for 60 min with and without catalyst.

Sample	Elemental compositions (wt.%)				HHV[a] (MJ/kg)
	C	H	N	O[b]	
Oil palm shell	50.01	7.66	13.31	29.02	22.43
WS, no catalyst	61.28	8.14	2.83	27.75	27.1
10% K_2CO_3	65.67	8.27	1.74	24.32	29.36
10% Na_2CO_3	69.47	7.84	0.37	22.32	30.37
10% NaOH	79.33	7.16	1.17	12.34	34.47
Bio-oil, no catalyst	79.43	6.28	0.96	13.33	33.08
10% K_2CO_3	80.69	6.73	0.81	11.77	34.41
10% Na_2CO_3	76.5	7.12	0.53	15.85	32.85
10% NaOH	69.86	8.13	0.51	21.5	31.06

[a] Higher heating value calculated by the Dulong Formula.
[b] By difference and assuming negligible sulfur content.

Table 5
Typical identification of compounds in bio-oil and water soluble products by GC–MS analysis at 603 K for 60 min.

No.	Name of compound	wt.% of bio-oil				wt.% of water soluble			
		No catalyst	10% K_2CO_3	10% Na_2CO_3	10% NaOH	No catalyst	10% K_2CO_3	10% Na_2CO_3	10% NaOH
1	Cyclobutanol	–	–	–	–	6.3	–	39.0	11.7
2	Acetic acid, [(aminocarbonyl)amino]oxo	–	–	–	–	51.1	–	21.5	–
3	Cyclohexan-1,4,5-one-1- carboxylic acid	–	–	–	–	42.6	–	–	–
4	Hexadecanoic acid, methyl ester	–	–	–	–	–	31.5	--	--
5	Hexadecanoic acid, ethyl ester	–	–	–	–	–	26.5	–	–
6	9-Dodecenoic acid, methyl ester	–	–	–	–	–	26.5	–	–
7	9-Octadecenoic acid, ethyl ester	–	–	–	–	–	15.5	–	–
8	Allanoic acid	–	–	–	–	–	–	20.4	–
9	Pentadecanoic acid,2,6,10, 14-tetramethyl	–	–	–	–	–	–	19.1	–
10	Ethylene oxide	–	–	–	–	–	–	–	52.9
11	1-Methyldodecylamine	–	–	–	–	–	–	–	14.8
12	3,3-Dimethylamino-butan-2-one	–	–	–	–	–	–	–	20.6
13	1,2-Benenediol,4-methyl	–	37.6	34.0	72.7	–	–	–	–
14	4-Ethylcatechol	–	24.4	24.5	16.4	–	–	–	–
15	1,2-Benenediol,3-methoxy	–	13.5	–	–	–	–	–	–
16	Ethylene oxide	–	–	18.0	2.6	–	–	–	–
17	1,4-Benenediol,2-methyl	–	–	10.7	–	–	–	–	–
18	n-Hexadecanoic acid	53.73	–	–	–	–	–	–	–
19	6-octadecenoic acid	21.33	–	–	–	–	–	–	–
20	Oleic acid	25.94	–	–	–	–	–	–	–
21	Oxiranemethanol,(R)	–	3.8	–	–	–	–	–	–
22	3,5-Dihydroxytoluene	–	12.7	–	–	–	–	–	–
23	Methyl tetradecanoate	–	–	12.8	–	–	–	–	–
24	1,5-Dihydroxytoluene	–	–	–	8.3	–	–	–	–

analysis results of liquid products, phenolic compounds and their derivatives are the main products of bio-oil that were presented in Table 5. It is known that the decomposition of biomass produces various types of heavy compounds containing long chain carboxylic acids, phenolic compounds, long chain esters and hydrocarbons. As expected, the LPs contain a large number of different compounds, making them very difficult to be identified. Therefore, in this study, only main key compounds were identified. The identification of key compounds opens the possibility of comparing the impacts of different catalysts on conversion and LPs of OPS in subcritical water treatment. This comparison leads to the assumption of main reaction pathways of OPS decomposition. The typically identified compounds in the bio-oil and water soluble products of OPS decomposition at 603 K and 60 min are presented in Table 5. It is evident that the use of different types of catalysts has an important effect on the formation of various compounds in the liquid products.

5. Conclusions

The decomposition of OPS in subcritical water liquefaction in either the presence or the absence of catalysts such as K_2CO_3, Na_2CO_3, and NaOH has been performed successfully using a batch reactor. The addition of 10% NaOH to the subcritical water liquefaction resulted to the highest solid conversion and liquid product at 84% and 53.4% respectively and significantly lower gaseous product as compared to those with either other catalysts or without any catalyst at similar condition. Hence, this study has substantiated the feasibility of converting OPS to LPs using subcritical water in the presence of catalyst.

Acknowledgment

The authors gratefully acknowledge the financial support from the Ministry of Science, Technology and Innovation (Science Fund No: 03-01-05-SF0208) and Universiti Sains Malaysia (FRGS Grant and Research University (RU) grant no. 814004) that have made this work possible.

References

[1] A. Demirbas, Supercritical fluid extraction and chemicals from biomass with supercritical fluids, Energy Conversion and Management 42 (2001) 279–294.

[2] International Energy Agency (IEA), Available from world wide web: http://www.iea.org.taxbace/about/copyright 2008.

[3] H. Mazaheri, K.T. Lee, S. Bhatia, A.R. Mohamed, Subcritical water liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of catalysts, Bioresource Technology 101 (2010) 745–751.

[4] H. Mazaheri, K.T. Lee, S. Bhatia, A.R. Mohamed, Sub/supercritical liquefaction of oil palm fruit press fiber for the production of bio-oil: effect of solvents, Bioresource Technology 101 (2010) 7641–7647.

[5] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, Cellulose hydrolysis in subcritical and supercritical water, Journal of Supercritical Fluids 13 (1998) 261–268.

[6] M. Sasaki, T. Adschiri, K. Arai, Kinetics of cellulose conversion at 25 MPa in sub- and supercritical water, AICHE Journal 50 (1) (2004).

[7] S. Saka, K. Ehara, S. Sakaguchi, K. Yoshida, Fermentability of the water-soluble portion obtained by hot-compressed water treatment of lignocelluloses, The 2nd Joint International Conference on "Sustainable Energy and Environment" (2006) 21–23 November, Bangkok, Thailand, 2006.

[8] S. Karago, T. Bhaskar, A. Muto, Y. Sakata, Hydrothermal upgrading of biomass: effect of K_2CO_3 concentration and biomass/water ratio on products distribution, Bioresource Technology 97 (2006) 90–98.

[9] K. Ehara, S. Saka, Decomposition behavior of cellulose in supercritical water, subcritical water, and their combined treatments, Journal of Wood Science 51 (2005) 148–153.

[10] Y. Qian, C. Zuo, J. Tan, J. He, Structural analysis of bio-oils from sub-and supercritical water liquefaction of woody biomass, Energy 32 (2007) 196–202.

[11] L. Cheng, X.P. Ye, R. He, S. Liu, Investigation of rapid conversion of switchgrass in subcritical water, Fuel Processing Technology 90 (2009) 301–311.

[12] Wahyudiono, M. Sasaki, M. Goto, Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water, Chemical Engineering and Processing 47 (9-10) (2008) 1609–1619.

[13] A. Demirbas, Biomass resource facilities and biomass conversion processing for fuels and chemicals, Energy Conversion and Management 42 (2001) 1357–1378.

[14] G. Brunner, Near critical and supercritical water, part I. Hydrolytic and hydrothermal processes, Journal of Supercritical Fluids 47 (2009) 373–381, (N18).

[15] S.H. Khajavi, Y. Kimura, T. Omori, R. Matsuno, S. Adachi, Kinetics on sucrose decomposition in subcritical water, LWT—Food Science and Technology 38 (2005) 297–302.

[16] Malaysia Palm Oil Bord (MPOB), Malaysia palm oil statistics, Economics and industry Development Division, MPOB, Kuala Lumpur, 2009.

[17] Malaysia palm Oil Production Council (MPOPC), Accessed on 14th April 2006. Available from World wide web: http://www.mpopc.org.my.

[18] H. Mazaheri, K.T. Lee, S. Bhatia, A.R. Mohamed, Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: an optimisation study using response surface methodology, Bioresource Technology 101 (2010) 9335–9341.

[19] A. Kruse, A. Gawlik, Biomass conversion in water at 330–410 °C and 30–50 MPa. Identification of key compounds for indicating different chemical reaction pathways, Industrial and Engineering Chemistry Research 42 (2003) 267–279.

[20] C. Xu, N. Lad, Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water, Energy & Fuels 22 (2008) 635–642.

[21] N. Takeda, T. Adschiri, K. Arai, Cellulose hydrolysis in subcritical and supercritical water, Journal of Supercritical Fluids 41 (2000) 361–379.

[22] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant properties and synthesis reactions, Journal of Supercritical Fluids 39 (2007) 362–380.

[23] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant, 2. Degradation reactions, Journal of Supercritical Fluids 41 (2007) 361–379.

[24] W.H. Chen, P.C. Kuo, A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry, Energy 35 (2010) 2580–2586.

[25] A. Cağlar, A. Demirbas, Conversion of cotton cocoon shell to liquid products by supercritical fluid extraction and low pressure pyrolysis in the present of alkalis, Energy Conversion and Management 42 (2001) 1095–1104.